09/600913
534 Rec'd PCT/PTC 24 JUL 2000

"Automatic checking and regulation of cleaner baths by determination of alkalinity"

This invention relates to a process for the automatic checking and regulation of cleaner baths, whereby the free alkalinity and/or the total alkalinity of the cleaner bath is determined by way of a measuring and regulating parameter and, where necessary, adjusted by metering measures. The process has been conceived in particular for technical cleaner baths in the metalworking industry, such as in automobile manufacture. It permits the functionality of the cleaner bath, characterised by the parameter "alkalinity", to be monitored automatically and, where necessary, enables the cleaner bath to be replenished automatically, or by external request, or enables other bath-maintenance measures to be initiated. In particular, the process is conceived in such a way that the results of the determinations are transmitted to a location remote from the cleaner bath. In addition, it is possible for interventions to be made in the automatic measuring sequence from a location remote from the cleaner bath or for make-up metering or other bath-maintenance measures to be initiated. The "location remote from the cleaner bath" may be situated, for example, in a higher-level process-control system, in a central control station of the plant in which the cleaner bath is located, or even outside the plant.

The cleaning of metallic parts prior to continued processing thereof constitutes a standard task in the metalworking industry. The metallic parts may, for example, be contaminated with pigment grime, dust, abraded metal, anti-corrosion oils, cooling lubricants or reshaping aids. Prior to continued processing, in particular prior to an anti-corrosion treatment (for example, phosphatisation, chromatisation, anodisation, reaction with complex fluorides, etc) or prior to lacquering, such contaminants have to be removed by a suitable cleaner solution. Spray processes, immersion processes or combined processes are considered for this purpose.

Industrial cleaners in the metalworking industry are, as a rule, alkaline (pH values in the range above 7, for example between 9 and 12). The basic constituents thereof are alkalis (alkali metal hydroxides, carbonates, silicates, phosphates, borates) and also non-ionic and/or anionic surfactants. The cleaners frequently contain, as additional auxiliary components, complexing agents (gluconates, polyphosphates, salts of amino carboxylic acids, such as ethylenediamine tetraacetate or nitrilotriacetate, salts of phosphonic acids, such as salts of

hydroxyethane diphosphonic acid, phosphonobutane tricarboxylic acid, or other phosphonic or phosphonocarboxylic acids), anti-corrosive agents, such as salts of carboxylic acids having 6 to 12 carbon atoms, alkanolamines and foam inhibitors, such as alkoxylates, closed at the terminal groups thereof, of alcohols having 6 to 16 carbon atoms in the alkyl residue. Provided that the cleaner baths contain no anionic surfactants, cationic surfactants may also be used.

By way of non-ionic surfactants, the cleaners as a rule contain ethoxylates, propoxylates and/or ethoxylates/ propoxylates of alcohols or alkylamines having 6 to 16 carbon atoms in the alkyl residue, which may also be closed at the terminal groups thereof. By way of anionic surfactants, alkyl sulfates and alkyl sulfonates are widely used. Alkyl benzene sulfonates are also encountered, but they are disadvantageous from the environmental point of view. By way of cationic surfactants, cationic alkylammonium compounds having at least one alkyl residue having eight or more carbon atoms are particularly preferred.

The alkalis in the cleaner bath contribute to the cleaning capacity thereof. For instance, they saponify saponifiable contaminants, such as fats and thereby make the latter soluble in water. In addition, they contribute to the detachment of insoluble dirt from the surface of the metal by electrostatic repulsion, as a result of adsorption of OH ions rendering the surfaces negatively charged. As a result of reactions of this type, optionally also as a result of removal by entrainment, alkalinity is consumed, so that the cleaning effect diminishes with time. It is therefore conventional to check the alkalinity of the cleaning baths at certain times and, where necessary, to replenish the solution with new active substances or to renew it entirely. This examination is carried out either manually or by means of an automatic titrator locally. In this connection the alkalinity is generally checked by titration with a strong acid. The operating personnel assess the alkalinity on the basis of the acid consumption and take the necessary measures, such as bath replenishment or bath renewal. This currently conventional process assumes that operating personnel are present in the vicinity of the cleaning bath at the requisite checking times. The shorter the checking intervals that are desired, the greater are the demands made on the operating personnel for the check measurements.

From EP-A-806 244 a process is known for determining the pH of a solution automatically and for make-up metering of acid or lye automatically in the event of anomalies. The object thereof involves maintaining the pH of a stream of liquid at a predetermined value. Acid-base titration is not carried out using this process. In this case, it is necessary to check the functionality of the plant in situ. It is not possible to intervene from a remote location in the sequence of pH measurements and metering measures.

On the other hand, the present invention sets itself as an object the automating and documenting of the checking of cleaner baths by determination of the alkalinity in such a way that at least the results of the determination of alkalinity are stored on a data carrier and/or are output. The measuring device employed should preferably examine and calibrate itself and in the event of malfunction transmit an alarm signal to a remote point. Furthermore, it should preferably be possible to examine the functionality of the measuring device and the results of measurement from a remote point. Moreover, it should be possible for interventions to be made in the measuring sequence and in the bath-maintenance measures from a remote point. By virtue of the remote control desired, the effort expended by personnel on checking and regulation of the cleaner baths is to be reduced.

This object is achieved by means of a process for automatic determination of the alkalinity of one or more cleaning baths containing surfactant by acid-base reaction using an acid, whereby, subject to the use of a suitable measuring device under program control,

(a) a sample of specified volume is drawn from a cleaning bath,

(b) if desired, the sample is freed of solids,

(c) a selection is made as to whether free alkalinity and/or total alkalinity is to be determined,

(d) the sample is titrated by addition of an acid, or an acid is submitted and the latter is titrated with the sample,

(e) the result of the titration is output and/or stored on a data carrier and/or utilised as the basis for further evaluations.

The sample volume drawn in step (a) may be permanently programmed into the control part of the measuring device to be employed for the process. The magnitude of the sample

volume may preferably be changed from a remote location. Furthermore, the control program may be so designed that it makes the sample volume to be used dependent on the result of a preceding measurement. For instance, the sample volume may be selected to be larger, the lower the alkalinity of the cleaner bath. The accuracy of the determination of alkalinity may be optimised by this means.

When reference is made to a "remote location", for the present purposes this is to be taken to mean a location that is not in direct contact, or at least not in optical contact, with the cleaner bath. The remote location may be, for example, a central process-control system that checks and regulates the cleaner bath as a sub-task within the context of an overall process for surface treatment of the metallic parts. The "remote location" may also be a central control and observation point from which the overall process is checked and regulated and which is located, for example, in a room differing from that of the cleaner bath. However, a point outside the plant in which the cleaner bath is located also comes into consideration by way of "remote location". By this means it becomes possible for specialists who remain outside the plant in which the cleaner bath is located to examine and regulate the cleaner bath. As a result, it is necessary for specialist personnel to be detained substantially less frequently at the location of the cleaner bath.

Suitable data lines with which the results of the determinations of alkalinity and also control commands may be transmitted are known.

Between the drawing of the sample and the actual measurement, it may be desirable to free the sample of solids in the optional step (b). In the case of a cleaner bath that is only slightly charged with solids, this is not necessary. However, in the case of a solids content of the cleaner bath that is too high, valves pertaining to the measuring device may become clogged and sensors, such as electrodes may be contaminated. It is therefore advisable to remove solids from the sample. This may be effected automatically by filtration or by using a cyclone separator or a centrifuge.

In step (c) a selection is made as to whether the free alkalinity and/or the total alkalinity is to be determined. This may be input permanently into the program control sequence. For

instance, both the free alkalinity and the total alkalinity may be determined in one determination cycle. However, the program may also decide to determine one of these two values more frequently than the other. This may be the case, for example, when determinations carried out previously have shown that one of the two values changes more rapidly than the other. Of course, the choice of whether free alkalinity or total alkalinity is to be determined may also be made by means of an external request. For the present purposes, the expression "external request" is to be understood to mean that it is possible for interventions to be made in the automated determination sequence either by a higher-level process-control system or manually via a data line.

The terms "free alkalinity" and "total alkalinity" are not unambiguously defined and are handled differently by the various users. For instance, particular pH values may be defined, up to which titration has to be effected in order to determine either the free alkalinity or the total alkalinity, for example pH = 8 for free alkalinity, pH = 4.5 for total alkalinity. These preselected pH values have to be input into the control system for the automatic determination process. As an alternative to particular pH values, the transition points of certain indicators may also be selected with a view to establishing the free alkalinity and the total alkalinity. Alternatively, turning-points in the curve of pH values may be selected and defined as end points for the free alkalinity or the total alkalinity.

With a view to actual determination of the alkalinity in step (d), use is made of the acid-base reaction with an acid. A strong acid is preferably selected for this purpose. In this connection, the sample may be titrated by addition of an acid until the specified criteria either for free alkalinity or for total alkalinity are attained. Alteratively, the acid may be submitted and titrated with the sample.

The result of the titration is subsequently output and/or stored on a data carrier (step (e)). In this connection, the data carrier may be situated at the location of the determination or in a remote arithmetic logic unit. The expression "output of the result of the titration" is to be understood to mean that the result is either passed on to a higher-level process-control system or is displayed on a screen or printed out in a recognisable manner. In this connection, the location of the display or the output of the result may be the "remote location" defined

above. Preferably, the results of the individual determinations are stored on a data carrier at least for a specified time interval, so that they may subsequently be evaluated, in the sense of quality assurance, for example. However, the results of the determinations of alkalinity do not have to be output or stored on data carriers immediately. Instead, they may also be utilised directly as the basis for further calculations, the results of these further calculations being displayed or stored. For instance, instead of the current alkalinity value in each case, the trend of the alkalinity values and/or the relative change thereof may be displayed. Alternatively, the current alkalinity values may be converted into "% of nominal content".

In the simplest case, the process according to the present invention operates in such a way that steps (a) to (e) are repeated after a specified time interval. This specified time interval depends on the requests of the operator of the cleaning bath and may comprise any time interval in the range from about five minutes to several days. For quality assurance it is preferable that the specified time intervals lie, for example, in the range between five minutes and two hours. For instance, a measurement may be carried out every 15 minutes.

However, the process according to the present invention may also be implemented in such a way that steps (a) to (e) are repeated after time intervals that are shorter, the more the results of two consecutive determinations differ. The control system for the process according to the present invention may also decide itself whether the time intervals between the individual determinations are to be shortened or lengthened. Of course, the control system has to be provided in advance with an instruction as to which time intervals are to be selected for which differences between the results of consecutive determinations.

Moreover, the process according to the present invention may be implemented in such a way that steps (a) to (e) may be carried out at any time by means of an external request. As a result, immediate checking, for example of the alkalinity content of the cleaner bath, may be undertaken if quality problems are established in subsequent process steps. Measurement of the alkalinity may also take place in a time-controlled manner (in accordance with fixed time intervals) or in an event-controlled manner (in the event of established changes or as a result of external requests).

The process according to the present invention is preferably implemented in such a way that the measuring device employed checks itself and, where necessary, recalibrates itself. To this end, provision may be made such that, after a specified time interval or after a specified number of determinations or by reason of an external request, the functionality of the measuring device employed is examined by check measurements of one or more standard solutions. For the purpose of examination, a standard solution having known contents of free and total alkalinity is titrated. This examination is closest to reality if a standard cleaner solution is employed by way of standard solution, the composition of which approximates as closely as possible to the cleaner solution to be examined. The standard solutions are preferably maintained subject to exclusion of air or under a protective gas (nitrogen, for example).

A central issue when examining the functionality of the measuring device is constituted by the checking of the sensor employed. For instance, the latter may be a pH-sensitive electrode, in particular a glass electrode. With the aid of a buffer solution by way of standard solution, it is possible to examine whether the electrode is supplying the expected voltage, whether it responds within the expected time and whether the slope thereof (= change in voltage as a function of the change in pH) lies within the nominal range. If this is not the case, the measuring device outputs an alarm signal locally or, preferably, at a remote location. This alarm signal may contain a suggestion for intervention that is selected by the control program of the measuring device or by the higher-level process-control system. For instance, it may be suggested that the electrode be cleaned or exchanged.

In the process according to the present invention there may also be provision such that the functionality of the measuring device employed is examined by check measurement of one or more standard solutions if the results of two consecutive measurements differ by a specified amount. By this means it is possible to distinguish whether established anomalies in the alkalinity of the cleaner bath are real and require bath-maintenance measures or whether they are being simulated by an error in the measuring system.

Depending on the result of the examination of the measuring device employed, the determinations of alkalinity that have taken place between the current check measurement and

the preceding one may be provided with a status identifier that denotes the reliability of these determinations of alkalinity. If, for example, consecutive check measurements for the purpose of examining the measuring device employed have shown that the latter is operating correctly, the determinations of the alkalinity may be provided with a status identifier "OK". If the results of the check measurements differ by a specified minimum amount, the determinations of the alkalinity that have taken place in the meantime may, for example, be provided with the status identifier "dubious".

Furthermore, provision may be made such that, depending on the result of the examination of the measuring device employed, automatic determination of the alkalinity is continued and/or one or more of the following actions are carried out: analysis of established anomalies, correction of the measuring device, termination of the determination of alkalinity, transmission of a status signal or an alarm signal to a higher-level process-control system or to a monitoring device - that is to say, to a remote location. Accordingly the measuring device may, if desired, decide, in accordance with specified criteria, whether it is operational to such an extent that the determinations of alkalinity may be continued or whether anomalies are established that necessitate manual intervention.

Various sensors are suitable for tracking the acid-base reaction of the cleaner solution with the acid employed for the titration. In accordance with the present state of the art, use will preferably be made of a pH-sensitive electrode, such as a glass electrode. The latter supplies a pH-dependent voltage signal which may be evaluated further. The use of an electrode of this type is particularly straightforward in terms of apparatus and is therefore preferred.

However, with a view to tracking the acid-base reaction of step (d), use may also be made of an indicator, the pH-dependent interaction of which with electromagnetic radiation is measured. For instance, this indicator may be a classical color indicator, the change in color of which is measured photometrically. Alternatively, use may be made of an optical sensor. In this connection it is, for example, a layer of an inorganic or organic polymer having a fixed dyestuff that changes color at a certain pH. The change in color is based, as in the case of a classical color indicator, on the fact that hydrogen ions or hydroxide ions that are able to diffuse into the layer react with the dyestuff molecules. The change in the optical

properties of the layer may be determined photometrically. Alternatively, films, such as organic polymers, may be used, the refractive index of which changes as a function of the pH. If, for example, a light guide is coated with such a polymer, it is possible to ensure that total reflection occurs in the light guide on one side of a threshold value of the refractive index, so that a ray of light is transmitted. On the other side of the threshold value of the refractive index, however, total reflection no longer occurs, so that the ray of light exits the light guide. At the end of the light guide it is then possible to detect whether the light is being propagated by the light guide or not. A device of this type is known as an "optrode".

Furthermore, inorganic or organic solids, the electrical properties of which change with the pH of the surrounding solution, may be employed as sensors. For instance, use may be made of an ion conductor, the conductivity of which depends on the concentration of the H^+ or OH^- ions. By measurement of the d.c. or a.c. conductivity of the sensor, it is then possible for the pH of the surrounding medium to be inferred.

The measuring system employed in the process according to the present invention is preferably designed such that it automatically monitors the filling levels and/or the consumption of the reagents employed (acids, standard solutions and test solutions, possibly auxiliary solutions) and, in the event of a specified minimum filling level not being attained, outputs a warning signal. By this means it is possible to prevent the measuring device from becoming non-functional as a result of lacking the necessary chemicals. Monitoring of the filling levels may be effected using known methods. For instance, the vessels with the chemicals may be situated on a balance that registers the respective weight of the chemicals. Or use may be made of a float. Alternatively, a minimum filling level may be examined by means of a conductivity electrode that is immersed in the vessel containing the chemical. The warning signal to be output by the measuring device is preferably transmitted to the remote location, so that the appropriate measures may be initiated from there. In general, provision is preferably made in the process according to the present invention such that the results of the determinations and/or of the check measurements and/or of the calibrations and/or the status signals are transmitted to a remote location continuously or at specified time intervals and/or on request. By this means, monitoring personnel that do not have to be present at the location of the cleaner bath are kept constantly informed of the current

alkalinity content thereof. Depending on the results of the determinations and of the check measurements, necessary corrective measures may be taken either automatically via a process-guidance system or as a result of manual intervention.

In the event of a specified minimum value of the alkalinity (free and/or total alkalinity) not being attained or on external request, the simplest corrective measure involves a device being activated that meters one or more replenishing components (solution or powder) into the cleaning bath. This may be effected, for example, in an automated manner in such a way that, depending on the alkalinity content ascertained, a certain quantity of replenishing solution or replenishing powder is supplied to the cleaning bath. In this regard, the magnitude of the added portion itself or, in the case of firmly specified added portions, the time intervals between the individual additions may be varied. This may be effected, for example, with the aid of metering pumps or in a weight-controlled manner. In the process according to the present invention there is provision, on the one hand, such that in the event of certain deviations from the nominal value (particularly if the functionality of the measuring device is established by the check measurements), a certain quantity of replenishing component is metered into the cleaning bath in order to make it up. On the other hand, however, this make-up metering may also be undertaken by reason of an external request, from a remote location for example, irrespective of the current alkalinity content.

In another embodiment of the present invention the cleaning bath is replenished in a throughput-dependent manner using a specified quantity of replenishing component per unit passed through (basic metering). For instance, in the case of a cleaning bath for automobile bodies the quantity of replenishing component that is added per cleaned body may be established. The checking, in accordance with the present invention, of the alkalinity then serves to check and to document the success of this specified addition and also, by means of additional event-dependent fine metering (additional metering in the event of the nominal values not being attained, suspension of the basic metering in the event of the nominal values being exceeded), to achieve a more constant mode of operation of the cleaning bath. By this means, fluctuations in quality are reduced.

Of course, the process according to the present invention assumes that the appropriate device

is made available. The latter includes a control system, preferably a computer control system, which controls the course of measuring in a time-dependent and/or event-dependent manner. It must furthermore include the necessary reagent vessels, pipelines, valves, metering and measuring devices etc for regulation and measurement of the sample streams. The materials should be adapted to the intended use, for example they should consist of high-grade steel and/or synthetic material. The control electronics of the measuring device should comprise an appropriate input-output interface, in order to be able to communicate with a remote location.

The process according to the present invention makes it possible, on the one hand, to check the alkalinity of cleaning baths in situ and to initiate specified corrective measures without manual intervention. By this means the process safety is enhanced and a constantly reliable cleaning result is achieved. Deviations from the nominal values may be detected at an early stage and corrected automatically or manually before the cleaning result is impaired. On the other hand, the measured data are preferably transmitted to a remote location, so that operating or supervising personnel are kept constantly informed of the state of the cleaning bath also when it is not located in the immediate vicinity thereof. The effort expended by personnel on checking and regulation of the cleaning bath may be considerably reduced by this means. By virtue of the documentation of the data collected in the process according to the present invention, the requirements of modern quality assurance are taken into account. The consumption of chemicals may be documented and optimised.